

## PRODUCTION OF SUPERCONDUCTOR/CARBON BICOMPONENT FIBERS

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Certain materials are unable to be drawn or spun into fiber form due to their improper melting characteristics or brittleness. However, fibrous samples of such materials are often necessary for the fabrication of intricate shapes and composites. In response to this problem, researchers at Clemson University developed and patented a unique process, referred to as the "piggyback process", to prepare fibrous samples of a variety of nonspinnable ceramics.<sup>1</sup> In this technique, specially produced C-shaped carbon fibers serve as "micromolds" to hold the desired materials prior to sintering. Depending on the sintering atmosphere used, bicomponent or single component fibers result.

While much has been demonstrated worldwide concerning the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  superconductor, fabrication into unique forms has proven quite difficult. However, a variety of intricate shapes are necessary for rapid commercialization of the superconducting materials. Researchers at Clemson University are currently investigating the potential for producing fibrous samples of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound by the piggyback process.

The carbon fibers employed for this research were melt spun in house from Amoco petroleum pitch, oxidized, and carbonized to produce high purity fibers with an approximate web distance of 30 microns and a length of 1-2 inches. The  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  powders were prepared by combining stoichiometric amounts of  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and  $\text{CuO}$ , calcining in air to  $\sim 900^\circ\text{C}$ , and sintering in flowing oxygen to  $950^\circ\text{C}$ . Samples were analyzed for purity using X-ray diffraction and a standard four-probe electrical resistivity measurement. An average transition temperature of  $\sim 90\text{K}$  was obtained.

Various organic and acrylic materials were investigated to determine suspending ability, reactivity with the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound during long term storage, and burn out characteristics. It was found that several of the tested materials reacted with the copper ions present in the compound and sufficiently altered the stoichiometry such that superconductivity was lost. The best suspension was produced from a mixture of superconducting powder ( $\leq 37\mu\text{m}$ ) with polyvinyl butyral in ethanol.

Carbon fibers coated with the various suspensions were subjected to low temperature firings ( $< 400^{\circ}\text{C}$ ) in air to burn out the organic radicals present. To retain the flexibility, strength, and protection of the carbon backbone, the composite fibers were subsequently fired to  $950^{\circ}\text{C}$  in an inert atmosphere to sinter the ceramic. During a series of thermogravimetric analyses of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound in inert atmospheres, it was discovered that a significant amount of oxygen is released from the structure at high temperatures. A slightly smaller quantity of oxygen was found to be released during processing in oxidizing atmospheres. However, in the presence of flowing oxygen or air, the lost oxygen is easily regained during slow cooling. Results indicated that the majority of this oxygen was "picked up" in the temperature range of  $650^{\circ}\text{C}$ - $300^{\circ}\text{C}$ . As unprotected carbon can withstand up to  $450^{\circ}\text{C}$  in oxidizing atmospheres, a low temperature anneal in flowing oxygen was employed to restore oxygen to the superconducting structure after inert atmosphere processing.

However, the oxygen released from the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound at high temperatures reacted with the unprotected carbon fiber, resulting in the formation of a carbon monoxide atmosphere along the interfacial area. The presence of carbon monoxide served to further reduce the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound over time. Due to their unique valency configuration, the copper ions were found to reduce most readily, and patches of copper were visible on the fiber surface after the inert atmosphere processing. The low temperature oxygen anneal produced an insulating layer of  $\text{CuO}$  along the fiber surface. The formation of this black layer of  $\text{CuO}$  was indiscernable from the normal superconducting black layer on sight but was evident by resistivity measurements and energy dispersive X-ray analysis (EDAX).

To substantiate these results, bulk materials of high purity graphite and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  were placed in contact and heated to  $950^{\circ}\text{C}$  in an inert atmosphere. After holding two hours at the peak temperature, a significant layer of copper metal was present at the interface. EDAX results confirmed that the stoichiometric copper content of the material was incrementally changed throughout the bulk material. Superconductivity could not be restored in the sample, even after processing in flowing oxygen for 5 hours at  $950^{\circ}\text{C}$ .

To eliminate interfacial reactions, a number of potential barrier layers were proposed, including silicon carbide, gold, silver, copper, and nickel. At present, however, only the use of nickel has been studied in depth. For preliminary experiments, thin foils of nickel were placed between bulk superconductor and graphite materials, and the samples were heated in an inert atmosphere to  $950^{\circ}\text{C}$ . No visible copper migration occurred, suggesting the interfacial reaction was significantly impeded. The small amount of oxygen released from the

superconductor was restored by a low temperature anneal in flowing oxygen. The resulting superconductor sample was found to exhibit the Meissner effect, and its composition was confirmed by X-ray diffraction.

To employ these results with fibrous samples, a thin, dense coating of nickel was applied to the carbon fiber surface using an electroless technique. Fibers treated with the electroless coating were filled with the superconductor suspension and heat treated in the same manner as before. No visible copper migration was present after inert atmosphere processing. Following a low temperature oxygen anneal, the fibers were examined using a Debye-Scherrer camera for small sample powder diffraction. Results indicated that the orthorhombic, superconducting phase of the compound was present (i.e. by the presence of a double peak at  $\sim 59^\circ$ ).

However, proper four point probe electrical measurements of the fibers have proven quite difficult and nonreproducible. Small microcracks have been discovered by electron microscopy, possibly resulting from a thermal expansion mismatch or an improper rate of heating or cooling. In addition, the resulting superconducting material is fairly porous, due to only short term soaks at the peak temperature and the burn out of the large amount of liquids required to produce the stable suspension. Both microcracking and porosity have been targeted to decrease overall critical current density in the superconducting materials. Therefore, the passing of very small currents through the fibers (i.e.  $\leq 1$  nA) may result in a reproducible measurement. At present, the smallest current passed through the samples has been on the order of 1mA. Nevertheless, for commercial applications, the bicomponent fibers must exhibit a much higher critical current density than this indicates.

While many questions have been answered with respect to the interfacial reactions between  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and carbon, much work is still necessary to improve the quality of the sintered material if the fibers produced are to be incorporated into useful composites or cables. Additional research is necessary to (1) evaluate the quality of the barrier layer during long soakings at the peak temperature; (2) adjust the firing schedule to avoid microcracking and improve densification; and (3) increase the solids loading in the superconductive suspension to decrease porosity.

## References

- <sup>1</sup> N. Mack, "The Piggyback Process for Forming Ceramic Fiber and Ceramic/Carbon Bicomponent Fibers", Master's Thesis, Clemson University, Clemson, SC, 1987.

## Acknowledgements

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## Figures

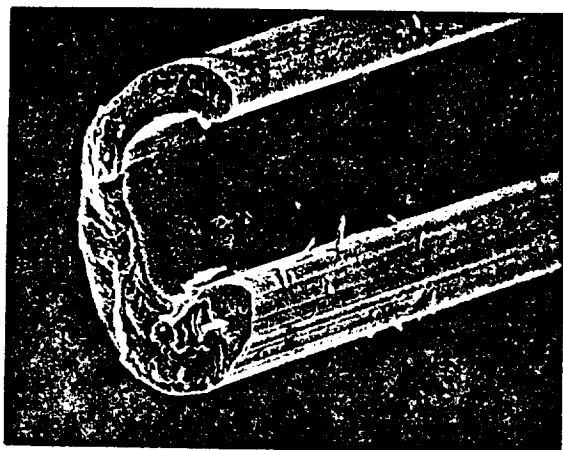


Figure 1. Electron micrograph of melt spun C-shaped carbon fiber

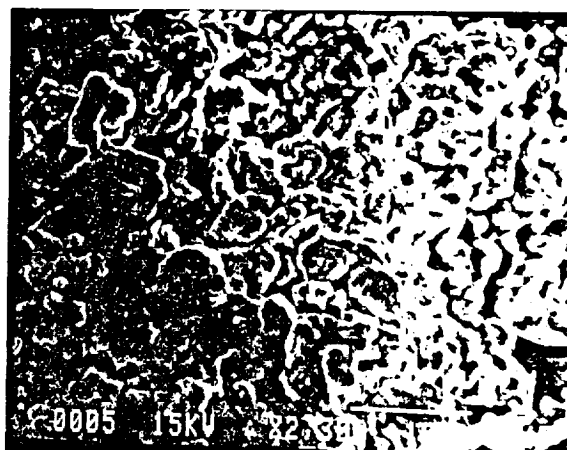


Figure 2. Electron micrograph of porous superconductor powder sintered inside the carbon fiber

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